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<p>(54) Title: OPEN CELL FOAM STRUCTURES, CATALYSTS SUPPORTED THEREBY AND METHOD OF PRODUCING THE SAME</p>		
<p>(57) Abstract</p> <p>This invention relates to highly porous open cell (3) foam structures (1) and to methods of preparing these highly porous open cell (3) foam structures (1) for use in improved catalytic systems. More specifically, this invention relates to highly porous open cell (3) foam structures (1) comprising open cell (3) foam structures (1) having a three-dimensional array of interconnected micro-rods (2). The micro-rods (2) comprise an inner core material integrally bonded to a porous outer layer wherein the porous outer layer comprises a material having a substantially higher porosity than the inner core material.</p> <div data-bbox="698 1134 1380 1701"> </div>		

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**OPEN CELL FOAM STRUCTURES, CATALYSTS SUPPORTED
THEREBY AND METHOD OF PRODUCING THE SAME**

5

FIELD OF THE INVENTION

This invention relates to highly porous open cell foam structures, to catalysts supported thereby and to methods
10 of producing the same.

BACKGROUND OF THE INVENTION

In order to reduce or overcome the problems of environmental pollution caused by pollutants such as
15 carbon monoxide, nitrogen-oxide compounds and toxic organic compounds that are produced in the exhaust of power plants or transportation vehicles, a need exists to provide catalytic processing equipment which removes or reduces the level of these noxious components. For this
20 purpose, it is important to create catalytic systems that can withstand high temperatures so that it is possible to reduce the overall dimensions of the catalytic system and diminish the power consumption, while still realizing effective catalytic removal of the noxious components.

25

Effective catalytic systems are also required for preventing the build-up of hydrogen in nuclear power plants. Typically, excessive hydrogen levels may be reduced by using devices employing high temperature
30 catalytic systems or flames. Unfortunately, devices that use high temperature systems or flames to reduce the excessive hydrogen levels, instead of reducing the risk, may actually increase the risk of a hydrogen explosion under certain circumstances.

Catalysts or catalyst supports based on open cell foam structures are known; J. Brockmeyer and J.F. Pizzirusso, "Ceramic Foam Offers Surprising Properties," J. Materials Engineering, pp. 39-41, July 1988; J. McCallion, "New
5 Materials, Applications Enter Booming Ceramic Scene," pp. 23, May 1988; and Antsiferov, V.N., Kundo, N.N., Ovchinnikova, V.E., Nokhrina, T.F., Porozova, S.E. and Fedorov, A.A., "Methane Conversion Catalyst Support Produced by Means of Powder Metallurgy," Russian J.
10 Appl. Chem., 1990, No. 9, pp. 1999-2003. Open cell foam structures having an interconnected open cell structure may have a porosity of up to 99% and a permeability for liquid and gas substances of up to 10^{-8} m², Antsiferov, V.N., Ovchinnikova, V.E., Porozova, S. Ya., Fedorova, E.
15 F.; "Highly Porous Cellular Ceramic Materials," Styeklo e Kyeramika, 1986, pp. 19-20.

Open cell foam structures may be prepared by using a reticulated polymeric foam as a substrate, e.g.,
20 reticulated polyurethane foam. Reticulated foam substrates are disclosed, for example, in U.S. Patent No. 3,946,039. In the first step, a layer of ceramic or metallic material is deposited on the exposed surfaces of the reticulated foam substrate. This deposition step may
25 employ a variety of known techniques such as slip casting, chemical plating or galvanic plating. The open cell foam structure is produced by heating the reticulated polymeric foam substrate containing the layer of ceramic or metallic material, which results in
30 destruction and removal of the reticulated polymeric foam substrate, e.g., by evaporation. Agglomeration, e.g. by sintering, of the ceramic or metallic particles during the heat treatment produces a structure that may be considered to be an analogue of the original reticulated
35 polymeric foam. That is, the network of pores and open cells present within the structural framework of the original reticulated polymeric foam is converted into a

product having a three dimensional array of interconnected micro-structural elements forming the edges of the cells in the open cell foam structure.

These micro-structural elements are herein referred to as
5 micro-rods.

The surface of the micro-rods forming the open cell foam structures normally appears smooth and is not very porous because the sintering processes typically used to produce
10 these structures lead to surface configurations having a minimum free energy level, and thus, to surfaces having a low specific surface area. If such open cell foam structures are used as catalysts or as catalyst supports, the smooth surfaces of these micro-rods are considered to
15 be a substantial drawback. This is generally understood to be due to the fact that heterogeneous catalysis becomes much less effective on surfaces having a low specific surface area.

20 Higher catalytic reactivity can be realized if the materials comprising the micro-rods that form the open cell foam structures have micropores which constitute 20% to 80% of the total volume of the micro-rods. Highly porous micro-rods having a surface micro-structure with a
25 high specific surface area have a high capacity for water absorption. Since the catalytic effectiveness of a porous catalytic surface may be generally correlated with water absorption capacity of the surface, a high water absorption is indicative of more effective catalytic
30 functioning. Unfortunately, open cell foam structures having micro-structural elements with 20-80% porosity have poor structural strength; Great Britain Patent No. 1,388,912 (1975).

35 It is known that reactivity of the catalyst can be enhanced by depositing a support layer, such as γ -aluminum oxide on an open cell structure, (U.S. Patent

No. 3,565,830). The layer of γ -aluminum oxide is characterized by a highly developed surface structure with a specific surface area of up to 100 m²/g. The high specific surface area provides for effective pick-up of the reactive components and for a high-quality dispersion of the active catalytic component. For open cell foam structures, however, because of the smooth surfaces and the low capacity for water absorption, the deposited carrier layer tends to be too thin, discontinuous and poorly adherent to the smooth surface. This layer is easily peeled off as a result of large or abrupt temperature changes.

Another problem of existing catalytic systems relates to the fact that carbon monoxide is one of the main contaminants of emission gas mixtures produced by transportation vehicles and power plants. Until now, catalysts formed from platinum or palladium, or alloys thereof, have been considered to be the most effective catalysts for removing CO, by oxidation, from emission gas mixtures. The high cost of platinum- and palladium-containing materials can make the gaseous decontamination equipment quite expensive. The development of lower cost non-platinum or non-palladium catalysts for CO oxidation could produce significant cost savings for programs directed toward reducing environmental pollution.

ADVANTAGES AND SUMMARY OF THE INVENTION

An object of the present invention is to provide highly porous open cell foam structures which overcome the above-mentioned problems of prior art catalytic systems.

More specifically, an object of the present invention is to provide highly porous open cell foam structures having both high structural strength as well as highly porous surfaces having a high specific surface area.

Still another object of the present invention is to provide a convenient and reliable method for preparing open cell foam structures suitable for use in catalytic systems.

5

Yet another object of the present invention is to provide high porosity catalytic systems having both high strength and high catalytic activity at high reagent flow rates.

10 A specific advantage of the present invention is that catalysts based on highly porous open cell copper foam structures can be produced which may be as effective as much more expensive platinum- or palladium-containing catalysts.

15

Yet another advantage of the present invention is that an open cell foam structure with a highly porous surface microstructure may be used either as a catalyst support or as the catalyst itself.

20

Still another advantage of the present invention is that catalytic systems based on open cell foam structures may be used to catalytically reduce excessive hydrogen levels without using high-temperature or flame-containing
25 devices.

Another advantage of the present invention is that high efficiency catalytic systems can be produced that have high reaction rates due to high burning temperatures.

30

Still another advantage of the present invention is that a non-channeled open cell porous structure may be used as a physical filter to effectively trap noxious reagents.

35 These and still other objects and advantages can be achieved with an open cell foam structure having a three dimensional array of interconnected micro-rods forming

the edges of the open cells of the open cell structure, the micro-rods having an inner core integrally bonded to a porous outer layer, the inner core comprising a first material and the porous outer layer comprising a second material, wherein the second material has a substantially higher porosity than the first material.

The open cell foam structures of the present invention may be formed by a method comprising preparing a first slip composition containing a first solvent, a first binding agent and a first ceramic material; coating a reticulated polymeric foam with the first slip composition to produce a coated polymeric foam having a first layer on the exposed surfaces of the reticulated polymeric foam; drying the coated polymeric foam to produce dried blanks of the coated polymeric foam; preparing a second slip composition containing a second solvent, a second binding agent, a second ceramic material and a pore-forming additive; coating the dried blanks with the second slip composition to produce a doubly-coated polymeric foam having a two-layer coating on the exposed surfaces of the polymeric foam; and heating and sintering the doubly-coated polymeric foam to form a highly porous open cell foam structure.

Alternatively, a highly porous metallic open cell foam structure may be prepared by a method comprising preparing a open cell foam structure wherein the structure comprises a three dimensional array of interconnected micro-rods forming the edges of the open cells of the open cell structure; oxidizing the surface of the micro-rods to form a porous surface microstructure that forms on the outer layer of micro-rods, and reducing the porous surface microstructure with hydrogen to form a highly porous open cell foam structure. Preferably, for this embodiment of the subject invention, the micro-rods comprise copper.

In addition, a device for removing or reducing excessive hydrogen levels may be made by using a catalyst comprising a catalyst support; a carrier layer on the catalyst support; and a catalyst coated on the support layer; wherein the catalyst support comprises an open cell foam structure having a three dimensional array of interconnected micro-rods forming the edges of the open cells of the open cell structure, the micro-rods having an inner core integrally bonded to a porous outer layer, the inner core comprising a first material and the porous outer layer comprising a second material, wherein the second material has a substantially higher porosity than the first material. Preferably, for this embodiment of the subject invention, the micro-rods comprise nickel and chromium, the catalyst support comprises γ -aluminum oxide and the catalyst comprises platinum and rhodium.

Further objects and advantages of the subject invention will be apparent to those skilled in the art from the following detailed description of the disclosed highly porous open cell foam structures and the methods for producing highly porous open cell foam structures.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1. An illustrative representation of the localized microstructure of an open cell foam structure.

- 5 Fig. 2. Schematic illustrations of the triangular cross-sections of the micro-rods disclosed herein.

Fig. 3. A representative illustration of the compression strength (MPa) vs. the porosity of the inner core (curve 1) and vs. the ratio of the inner core
10 thickness to the total micro-rod thickness (curve 2).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

While the following description of preferred embodiments
15 of the present invention is intended to provide detailed instructions that would enable one of ordinary skill in the art to practice the invention, the scope of the invention is not to be limited to the scope of the specific product or process details hereinafter provided.

20

The basic unit of the macroscopic porous space of open cell foam structures may be generally represented by a cell that is typically shaped as a pentagon-dodecahedron. In terms of cubic symmetry, this corresponds to one of
25 the simple shape types for which the class is designated as m3. The coordination number, as determined by the number of adjacent neighbors for each given cell, is 12. A coordination number of 12 is evidence that the repeating units in the open cell foam structure are
30 characterized by a high packing density of polyhedron cells. Open cell foam structures, in general, have areas of local short-range order in the macroscopic structure formed by the polyhedron cells. Long-range order does not normally exist in the types of open cell foam
35 structures described herein.

The three-dimensional region of local short-range order

in open cell foam structures may typically have a size that includes four to five polyhedron cells. This results in channels being present in the structure wherein the channels may have a thickness which is 0.3 to
5 0.5 times as thick as the cell diameter. However, unlike normally ordered lattice structures (e.g. honeycomb structures) having long-range order with continuous straight-line channels aligned in parallel with the high order axes, the channels in the pore space structure of
10 open cell foam structures are typically built up from short straight-line channels which, on average, are 4 to 6 times as long as the cell diameter.


The herein-described channel-type porosity, which is
15 characteristic of the macroscopic structure of highly porous open cell foam structures, simultaneously accounts for the high permeability of highly porous open cell foam structures as well as for the reduced chance for the reactant materials, e.g. noxious components, to pass
20 through such structures without reacting. By properly controlling the effective channel dimensions so as to balance the competing needs of high permeability and high reactivity, such structures offer considerable promise for use as catalysts and as catalyst supports.

25 As noted above, the microstructural elements forming the edges of the cells of the open cell foam structure are herein referred to as micro-rods. The cross-sectional configuration of these micro-rods plays an important role
30 in affecting the overall physical properties, such as strength, water absorption, reactivity, etc., of the highly porous open cell structures. Each micro-rod typically has an axial pore of triangular cross-section. The axial pores are formed, as described below, by
35 removal of the reticulated polymeric foam substrate that may be used to produce the open cell foam structures. These axial pores form an inter-linked capillary system

inside the micro-rods, wherein the total volume occupied by the capillaries may be about 3 volume percent of the micro-rod volume. The axial pores are surrounded by a layer, or layers, of material having a porosity that is controlled according to the methods disclosed below. The present invention relates to methods of producing micro-rod cross-sectional configurations that result in highly porous open cell foam structures having use as improved catalysts or catalyst support systems. Fig. 1 shows the localized microstructure, as schematically represented in U.S. Patent No. 4,569,821, of an open cell foam structure (1) having micro-rods (2) forming the edges of the open cells (3). Figs. 2(a), 2(b) and 2(c) show schematic illustrations of the triangular cross-sections of the micro-rods disclosed herein. Fig. 2(a) shows the axial pore (4) and micropores (5) in the low porosity material, shown as (6) of Fig. 2(b), of the inner core. Fig. 2(b) shows the highly porous layer (7) that surrounding the inner core. Fig. 2(c) shows a carrier layer (8) on the highly porous layer with a catalyst layer (9) coated on the carrier layer.

The preferred method for making the highly porous open cell foam structures of the subject invention is slip casting. The slip casting process may be carried out using any of a large number of different methods. In the present illustrative method, a reticulated polyurethane foam is used as a substrate wherein the polyurethane foam is imbedded with what is generally referred to as a slip composition. The slip from the slip composition adheres to the exposed surfaces of the micro-structural elements of the reticulated polyurethane foam substrate. The slip composition may be a slurry or dispersion, for example, of a solvent containing particles of a starting material that is a ceramic or metal powder mixed or dispersed together with a binding agent. Preferably the binding agent is an organic binder. The slip composition may

include still other components such as a pore-forming additive. The solvent, which is not to react with the reticulated polymeric foam substrate or the pore-forming additive, may typically be water or ethanol.




5


The metals or ceramic materials that may be used as the starting materials in the present invention may include any of the very large number of metals and materials that have been used to produce porous metal or ceramic foam products. Such metals or ceramic materials include Cu, Ni, Fe, Mo, W, Ni-Cr alloys, Ni-Fe alloys, or other alloys thereof, stainless steel, porcelain, Al_2O_3 , SiO_2 , Mo_2C , WC or Cr_3C . The preferred metal of the present invention is copper, or an alloy of nickel and chromium, and the preferred ceramic material is porcelain.

The metallic or ceramic materials used to make the highly porous open cell foam structures may initially be in the form of a powder or particles, or any other form which may be used to produce highly porous foam products. These materials may be obtained from any of many known suppliers. The materials may be further characterized as being sphere-shaped particles to provide convenient fluidity and slip filling. Preferably the starting materials used to make both the first and the second slip compositions comprise materials having substantially the same ceramic or metallic composition.

The binding agents that may be used in the slip composition include polyvinyl alcohol and isopropanol. The preferred binding agent of the present invention is polyvinyl alcohol, which may be obtained from any of many known suppliers.



The reticulated polymeric foam substrate may be selected from many different polymers, including polyurethanes, polyureas, polyesters, polyamides, polyethers,



polystyrenes, polyvinyl chlorides, polyethylene or polypropylene. The preferred polymeric foam substrate is polyurethane foam.

5 The slip composition may be prepared by mixing the metal or ceramic starting material with the solvent and the binding agent to produce a slurry or dispersion. The reticulated polymeric foam substrate, for example, polyurethane foam, may be dipped or sprayed with the slip
10 composition and the excess slip composition is then removed before drying to produce dried blanks having a single layer of the slip on the exposed surfaces of the micro-structural elements of the reticulated polymeric foam substrate.

15 In one of the preferred embodiments of the present invention, a second slip composition is then prepared using substantially the same ingredients as above, but also including a pore-forming additive. The dried blanks
20 of the polyurethane foam having the single layer formed by the first slip composition may be dipped or sprayed with the second slip composition containing the pore-forming additive. The solvent is removed by drying to produce a polyurethane foam having a double coating on
25 the exposed surfaces of the polyurethane foam.

The doubly-coated polyurethane foam may then be heated to destroy and remove the polyurethane foam and the pore-forming additive and to sinter the ceramic or metallic
30 materials to form what is herein referred to as a highly porous open cell structure having a three dimensional array of interconnected micro-rods forming the edges of the open cells of the open cell structure. This heating and sintering may be carried out using many different
35 methods known in the art.

The pore-forming additive is typically an organic

constituent that is destroyed and removed with the reticulated polymeric foam. The pore-forming additive produces pores within the outer layer of the micro-rods. The pore-forming additives that may be used include
5 polystyrene, polyethylene and polymethyl methacrylate. The preferred pore-forming additive of the present invention comprises particles of polymethyl methacrylate. The particle size of the pore-forming additives may be
10 in average diameter. The preferred particle size is from about 20 microns to about 30 microns in average diameter. The weight percent of the particles of polymethyl methacrylate is from about 10 weight percent to about 90
15 weight percent of the total weight of the material used to form the outer layer of the micro-rods. Preferably, the particles of polymethyl methacrylate are substantially spherical.

The highly porous open cell structures produced using the
20 methods of the present invention comprise micro-rods having an inner core of a low porosity material surrounding an axial pore. The axial pore at the center of the micro-rod is produced by destruction and removal of the reticulated polymeric foam. The low porosity
25 material of the inner core is integrally bonded to an outer layer that is preferably comprised of substantially the same metallic or ceramic composition but having substantially higher porosity than the low porosity material in the inner core. The higher porosity of the
30 outer layer may be produced by use of pore-forming additives in the second slip composition. The degree of porosity may be varied by varying the weight percent of the pore-forming additive in the second slip composition. The low porosity material in the inner core described
35 herein refers to materials that have a porosity of about 0.5% to about 10% and the high porosity material of the outer layer refers to materials that have a porosity of

about 20% to about 80%. Most preferably, the high porosity material of the outer layer has a porosity of about 40% to about 70%.

5 The high porosity material of the outer layer provides the micro-rod with a highly porous surface microstructure. The highly porous surface microstructure is preferred for achieving effective heterogeneous catalysis. The low porosity material of the inner core
10 provides the micro-rod with strength and structural integrity. By appropriately controlling the total micro-rod thickness and the relative thickness and porosity of the low porosity material of the inner core and of the high porosity material of the outer layer, highly porous
15 open cell foam catalysts and catalyst supports may be produced having both high permeability and high reactivity with noxious components, while still retaining the high structural strength and integrity of a high capacity catalyst. Preferably the thickness of the
20 micro-rods is from about 0.1 mm to about 3 mm. Most preferably, the thickness of the micro-rods is from about 0.5 mm to about 2 mm. In addition, the inner core preferably has a thickness of about 60% to about 80% of the total micro-rod thickness, and the porous outer layer
25 preferably has a thickness of about 40% to about 20%, respectively, of the total micro-rod thickness.

An advantage of the present invention is that the highly porous surface layer of the micro-rod is integrally
30 bonded to the inner core of the micro-rod such that it cannot be easily peeled off as a result of large or abrupt temperature changes or rough handling. The adherence and integrity of the bonding of the high porosity material of the outer layer to the low porosity
35 material of the inner core may be strengthened by appropriate selection of the ceramic or metal materials used in the slip composition and by the heating and

sintering conditions used to produce the highly porous open cell foam materials. Preferably the starting materials of the first and second slip compositions are substantially the same except for addition of an
5 appropriate quantity of the pore-forming additive in the second slip composition.

The preferred ceramic composition of the present invention is porcelain. Porcelain is typically comprised
10 of SiO_2 , Al_2O_3 , CaO , MgO , TiO_2 , Fe_2O_3 , Na_2O and K_2O . The highly porous surface microstructure of porcelain micro-rods typically has a high specific surface area that provides for effective pick-up of reactive components as well as for high-quality dispersion of the active
15 catalytic component. The specific surface area of the catalytic support prepared from porcelain using the methods of the present invention is typically in the range from about 2.0 to about 10 m^2/g .

20 The highly porous open cell foam structures of the present invention may be used either as catalysts or as catalyst supports. Whenever the highly porous open cell foam structures are used as catalyst supports, the highly porous open cell foam structures may be combined with a
25 catalyst by covering the micro-rods of a metallic open cell foam structure with a support layer comprised of metal oxides such as Al_2O_3 , ZrO_2 or TiO_2 and then coating the surface of the support layer with a catalyst such as platinum, platinum-rhodium, palladium, cerium, Cu, Ni,
30 etc. The highly porous metallic open cell structures may be formed from metals such as Ni, Cr, Mo, Co, W, alloys thereof, or stainless steel.

In one of the preferred embodiments of the present
35 invention, it was discovered that a highly porous open cell foam structure of nickel-chromium metal coated with a support layer of γ -aluminum oxide, which was

impregnated with a finely dispersed layer of platinum-rhodium, was surprisingly effective as a hydrogen-oxidation catalyst at much lower temperatures than was typically observed for known hydrogen-oxidation catalysts.

In another of the preferred embodiment of the subject invention, it was discovered that highly porous open cell copper foam structures with micro-rods having an integrally-bonded structure may be made and employed as catalysts. In this case, however, it was discovered that a different method was preferred for producing highly porous open cell foam structures with adequate strength as well as effective catalytic activity. If a copper micro-rod structure was prepared using the slip casting method, wherein the micro-rods had a porosity of 20 to 50%, the compression strength of the material did not reach 0.4 MPa. Porous structures with such low compression strength are generally unsuitable for use as catalysts.

Alternatively, an open cell copper foam structure, initially having a low porosity throughout the micro-rods, may be prepared by chemical or electrochemical deposition of copper on a permeable open cell polyurethane foam. The porosity of the micro-rods prepared using this method may be in the range of 0.5 to 1% and the exposed surface of these micro-rod structural elements is smooth. The smooth surface results in a relatively low reactivity of this material even when used at higher temperatures as a catalyst for CO oxidation, as shown below:

<u>% oxidation</u>	<u>temperature °C</u>
25	270
50	310
75	340

5

Although there are techniques for providing a porous layer on the surface of the micro-rods, such as slip casting, chemical precipitation from a solution, etc., these techniques do not insure formation of a tight integral bond between the low-porosity inner core and the porous outer layer. These methods produce a detectable boundary interface between the two layers and, thus, do not achieve the integral bonding of the subject invention.

15

It was surprisingly found, however, that highly porous open cell copper foam structures with micro-rods having a low porosity inner core integrally bonded to a high porosity outer layer could be formed by a two-step oxidation-reduction process. In the first step, oxidation of an open cell copper foam structure having low porosity micro-rods may be carried out in air at temperatures from 300-800 °C to produce a structure having a high porosity outer layer on a low porosity inner core. Preferably, the oxidation is carried out at temperatures from 400-600 °C. If the oxidation temperature is too low, a sufficiently thick active outer layer is not formed and, thus, catalytic activity is too low. If oxidation is performed at too high a temperature, the oxidation is too great and causes an unacceptable loss in strength of the overall open cell copper foam structure.

After the oxidation step, a reduction step is carried out in the presence of hydrogen at temperatures about 200-300 °C less than the oxidation temperature. A reduction temperature that is too high causes sintering of the high

porosity outer layer and, thus, a loss in the active surface area and a reduction in catalyst efficiency. Using this two-step oxidation-reduction method, a high porosity outer layer is formed on and integrally bonded
5 to a low porosity inner core. Preferably, the porous outer layer is 20-40% of the micro-rod thickness and has a porosity of 50-80%. Preferably, the low porosity material of the inner core has a porosity of about 0.5 to about 3%. Most preferably, the low porosity material of
10 the inner core has a porosity of about 0.5 to about 1%.

This invention will now be described in detail with respect to the specific preferred embodiments thereof, it being understood that the materials and the process steps
15 of the following example are intended to be illustrative only and that the invention is not intended to be limited to the materials, conditions, process parameters and the like recited herein.

20 EXAMPLES OF THE INVENTION


The first example shows that the micro-rod structure of the present invention may be used to produce highly porous open cell foam structures having, unexpectedly, both high structural strength and high water absorption.
25 The high water absorption is indicative of high catalytic effectiveness. The second example relates to a method for preparing highly porous open cell foam structures having a micro-rod structure wherein the highly porous open cell foam structure is comprised of copper. The
30 third example shows how highly porous open cell structures having a micro-rod structure of the present invention may be prepared and used as a catalyst support.

Example 1

35 Polyurethane foam having an average cell diameter of 2.5-3 mm was cut to prepare blanks with dimensions of 35 x 35 x 25 mm. A porcelain compound obtained from Kamcable Co.

(Perm, Russia) and comprising 66.52% SiO_2 , 27.15% Al_2O_3 , 0.37% FeO_3 , 0.17% TiO_2 , 1.44% CaO , 0.73% MgO , 2.42% K_2O and 1.20% Na_2O was mixed with water and a binding agent, in this case, polyvinyl alcohol, to form a slip composition.

- 5 The polyvinyl alcohol had an average molecular weight of 500 and was obtained from Fluka Chemie A.G. (Switzerland).

- 10 The polyurethane foam blanks were soaked in the slip composition to coat the exposed surfaces of the polyurethane foam with slip. The excess slip was removed by squeezing and the blanks were allowed to dry to form dried blanks having a density of 0.1, 0.2, 0.3, 0.4 and 0.5 g/cm^3 , respectively. 

- 15 This process was followed by the preparation of a second slip composition containing substantially the same composition as the first slip composition, that is, a porcelain compound mixed in a water solution containing
20 polyvinyl alcohol, but which, in addition, also included a pore-forming additive, polymethyl methacrylate (PMMA). The particles of PMMA were 10 to 100 microns in size, predominantly 20 to 30 microns in size, and amounted to 15, 30, 50, 80 and 85 weight percent of the total
25 quantity of ceramic powder.

- Slip from the second slip composition was deposited on the dried blanks by dipping or spraying and the coated blanks were provided with a heat treatment that sintered
30 the materials to produce the highly porous open cell foam structures to be used as catalysts or catalyst supports. The heat treatment conditions were selected so as to provide a gradual burn-out of the polyurethane foam blanks and of the particles of PMMA used as the pore-
35 forming additive. The heat treatment was also intended to insure that the shape and permeability remained unchanged. To achieve these objectives, the highly

porous open cell foam structures prepared from the porcelain mixture were sintered at temperatures from 1320 to 1420 °C.

- 5 Analyses of the highly porous open cell foam structures with a scanning electron microscope demonstrated that the highly porous open cell foam structures produced by this method have a micro-rod structure without a visually detectable boundary interface between the low porosity
10 inner core and the high porosity outer layer.

To test the suitability of using these sintered materials as catalyst supports, they were measured for compression strength and for water absorption, as shown in Table 1.

TABLE 1

Sample No.	Layer Thickness (percent of total micro-rod thickness)		Layer Porosity (%)		Compression Strength (MPa)	Water Absorption (%)
	Inner Core	Outer Core	Inner Core	Outer Core		
1	50	50	5±1	50±5	0.5	7-10
2	60	40	5±1	50±5	1.0	7-10
3	70	30	5±1	50±5	1.17	5-7
4	80	20	5±1	50±5	1.2	5-7
5	85	15	5±1	50±5	1.25	2-5
6	70	30	5±1	50±5	1.17	2-5
7	70	30	5±1	15±5	1.17	5-7
8	70	30	5±1	20±5	1.17	5-7
9	70	30	5±1	50±5	1.15	12-15
10	70	30	5±1	87±5	1.13	10-12
11	0	100	--	50±5	0.4	5-7
12	100	0	5±1	--	1.25	1-2

The compression strength was measured by Instron universal testing equipment, (Instron Limited, England). The water absorption was measured by weighing. The data in Table 1 show that an outer layer thickness of about 5 20% to about 40% of the total micro-rod thickness does not, surprisingly, cause a substantial decrease in compression strength but still provides much higher water absorption than the open cell foam structures not having the high porosity outer layers. As shown in Table 1, an 10 outer layer thinner than about 20% of the total micro-rod thickness does not provide for good water absorption and an outer layer thicker than about 40% of the total micro-rod thickness causes an unacceptable decrease in strength.

15

If the porosity of the outer layer is less than about 20%, high catalytic reactivity cannot be achieved and if the porosity is greater than about 80%, the outer layer may be easily peeled off, thus causing catalytic 20 reactivity to decrease.

In comparison with other known open cell foam structures in which the micro-rods have a uniform porosity, the highly porous open cell foam structures of the present 25 invention maintain surprisingly high compression strength while still having high water absorption.

Fig. 3 shows the compression strength (MPa) plotted against the porosity (%) of the inner core (curve 1) and 30 against the ratio of the inner core thickness to the total micro-rod thickness (curve 2) for a porcelain open cell foam structure having an average cell size of about 2 mm and a density of about 0.5 g/cm³. An increase in porosity above about 10% for the inner core material 35 produces an unacceptable decrease in the overall strength of the highly porous open cell foam structure. A micro-rod thickness wherein the low porosity material of the

inner core is greater than about 60% of the total micro-rod thickness is required to achieve a material strength greater than about 2 MPa. A material strength of at least about 2 MPa is required for satisfactory

5 application of these materials as catalyst supports. As shown in Table 1, if the thickness of the inner core is greater than about 80% of the total micro-rod thickness, there is a reduction of outer layer porosity and this accounts for an unacceptable drop in water absorption.

10

Example 2

Samples of a highly porous copper open cell foam structure comprising micro-rods were prepared by first forming an open cell structure having a single-layer
15 micro-rod structure. In the first step, copper was chemically deposited on an open cell polyurethane foam. Dried blanks were prepared and then the dried blanks were heated and sintered at temperatures from about 500 to about 900 °C. The material in the single layer micro-rod
20 structure had a porosity of about 0.5 to about 1%.

These single-layer micro-rod open cell structures were then oxidized in air at a temperature from about 300 to about 500 °C for 1.4 hours. The oxidized open cell
25 structures were then reduced in hydrogen for about 1-3 hours at temperatures from about 200 to about 300 °C to produce highly porous copper open cell foam structures having a two-layer micro-rod structure. The high porosity outer layer had a thickness of about 20% to
30 about 40% of the total micro-rod thickness and a porosity of about 50% to about 80%. The low porosity material of the inner core retained the original porosity of about 0.5 to about 1%.

35 The catalytic reactivity was tested by means of a microcatalytic reactor. The stoichiometric catalytic conversion of CO to CO₂ by the subject catalyst was

compared with the catalytic reactivity of a surface on which a 0.3% layer of palladium had been deposited. The comparison was carried out using a helium carrier gas having a flow rate of 20-60 cm³/min. The output gas mixture was chromatographically analyzed using a method such as described in "Applied Industrial Catalysis, Vol. 1, edited by Bruce E. Leach, Conoco Inc. Research and Development, Poonca City, Oklahoma, 1983. The kinetic characteristics of this process are summarized in Table 2.

TABLE 2

Comparison of the catalytic kinetic characteristics for the oxidation of CO for a catalytic Pd-coated surface ("Pd") and for a highly porous Cu open cell foam structure ("Cu").

<u>Catalyst</u>	<u>Temperature</u> °C	<u>Volume</u> m ³ /s	<u>c</u> mole/m ³	<u>a</u>	<u>W x 10⁶</u> mole/m ³ /s
Pd	140	3.83 x 10 ⁻⁶	2.81	1.57	1.88
			5.70	1.19	2.89
			11.56	0.82	4.04
			29.17	0.57	7.08
Cu	130	3.68 x 10 ⁻⁶	2.46	4.42	3.64
			5.09	3.76	6.41
			10.70	2.74	9.81
			26.96	2.55	23.02

where a = transformation degree; c = average CO content in a pulse, mole/m³; W = average reaction rate, mole/m³/s

The initial temperature during CO oxidation on the copper-based catalyst was about 110 °C and about 90 °C for catalysts prepared using a one-cycle and a two-cycle oxidation-reduction process, respectively. The apparent
5 activation energy of the process equaled 77 KJ/mole for a highly porous open cell copper foam catalyst after a two-cycle oxidation-reduction process. In the case of a palladium-based catalyst, the corresponding data were found to be 100 °C and 64 KJ/mole, respectively. Thus,
10 the catalytic reactivity of a unit volume of the highly porous open cell copper foam catalyst using micro-rods was comparable to the catalytic reactivity level of the reference palladium catalyst.

15 Substitution of the relatively inexpensive highly porous micro-rod open cell copper foam catalyst for much more expensive platinum or platinum-family catalysts could provide substantial economic savings.

20 **Example 3**

A highly porous open cell foam structure having a micro-rod structure of a nickel-chromium alloy was prepared using the slip casting process. In this case the slip compositions were prepared from a mixture of nickel and
25 chromium powders wherein the nickel was about 82 weight percent of the total metal powder and chromium was about 18 weight percent. The powders had an average particle size of about five microns in diameter. These powders were mixed in water solutions wherein polyvinyl alcohol
30 was used as the binding agent. The pore-forming additive used to produce the porous outer layer of the micro-rod was polymethyl methacrylate.

The first slip composition was coated on a polyurethane
35 foam and then dried to produce dried blanks which were then coated with a slip composition containing the pore-forming additive. These doubly-coated blanks were then

processed in hydrogen at temperatures from about 1100 °C to about 1300 °C to produce highly porous open cell foam structures comprised of nickel-chromium micro-rods.

- 5 The nickel-chromium micro-rod surfaces were then coated with a carrier layer of γ -aluminum oxide by submerging the highly porous nickel-chromium open cell foam structure in a saturated solution of sodium aluminate at 60-70 °C for three hours. A layer of $\text{Al}(\text{OH})_3$ was
10 subsequently formed by swirling with distilled water until the hydrolysis reaction was completed. The specimen was then heated in air for three hours at about 500 °C to form a γ -aluminum oxide carrier layer having a thickness of about 60-100 microns and a specific surface
15 area of about 200 m^2/g . About 20 g/mm^2 of the γ -aluminum oxide adhered to the surface of the nickel-chromium micro-rods.

- A platinum-rhodium catalytic layer was then formed on the
20 surface of the γ -aluminum oxide carrier layer by impregnating the specimen in a 0.5% solution of platinum chloride and rhodium chloride and subsequently reducing at 60-80 °C in a 1% solution of sodium formate to produce a finely dispersed metallic layer of platinum-rhodium.
25 The content of platinum and rhodium was about 0.25 and 0.1 weight percent, respectively, as compared to the total weight of the catalyst.

- The catalytic activity of the specimen was measured using
30 a gas reactor and an infra-red spectrometer. The degree of conversion of CO into CO_2 was used to characterize the degree of catalytic activity. The measurements were carried out under pulse conditions using the SLONDI 64'1 method, which is described in "Applied Industrial
35 Catalysis," supra. The results were compared with the results obtained with a Volvo-740 catalytic converter after it had been used in an automobile that had traveled

about one thousand kilometers. The exhaust gases were measured at a gas mixture flow rate of 30 liters/hour.

The results in Table 3 show the high efficiency of CO-to-CO₂ conversion at low temperatures for the test samples as compared with the Volvo reference.

TABLE 3

The degree of conversion of CO to CO₂ at T(°C). The test sample was prepared according to Example 3 and the reference was a VOLVO-740 catalytic converter.

T (°C)	20	140	160	180	200	220	240	260	280	300
Test	33	48	53	57	60	66	74	83	93	98
Reference	4	8	12	50	69	80	100	100	100	100

WHAT IS CLAIMED IS:

1. A highly porous open cell foam structure comprising:
an open cell foam structure having a three dimensional array of interconnected micro-rods forming the edges of the open cells of said open cell structure, said micro-rods having an inner core integrally bonded to a porous outer layer, said inner core comprising a first material and said porous outer layer comprising a second material, wherein said second material has a substantially higher porosity than said first material.
2. The highly porous open cell foam structure of claim 1 wherein said first material comprises substantially the same ceramic or metallic composition as said second material.
3. The highly porous open cell foam structure of claim 1 wherein said first material has a porosity from about 0.5% to about 10%.
4. The highly porous open cell foam structure of claim 1 wherein said micro-rod has a thickness from about 0.1 mm to about 3.0 mm.
5. The highly porous open cell foam structure of claim 1 wherein said micro-rod has a thickness from about 0.5 mm to about 2.0 mm.
6. The highly porous open cell foam structure of claim 1 wherein said second material has a porosity from about 20% to about 80%.
7. The highly porous open cell foam structure of claim 1 wherein said second material has a porosity of about 40 to about 70%.

8. The highly porous open cell foam structure of claim 1 wherein said inner core has a thickness from about 60% to about 80% of the total micro-rod thickness and said porous outer layer has a thickness from about 40% to about 20% of the total micro-rod thickness.

9. The highly porous open cell foam structure of claim 2 wherein said ceramic or metallic composition comprises a composition selected from the group consisting of copper, porcelain, nickel and chromium.

10. A method for forming a highly porous open cell foam structure comprising:

- preparing a first slip composition containing a first solvent, a first binding agent and a first ceramic material;

- coating a reticulated polymeric foam with said first slip composition to produce a coated polymeric foam having a first layer on the exposed surfaces of said reticulated polymeric foam;

- drying said coated polymeric foam to produce dried blanks of said coated polymeric foam;

- preparing a second slip composition containing a second solvent, a second binding agent, a second ceramic material and a pore-forming additive;

- coating said dried blanks with said second slip composition to produce a doubly-coated polymeric foam having a two-layer coating on said exposed surfaces of said polymeric foam; and

- heating and sintering said doubly-coated polymeric foam to form a highly porous open cell foam structure.

11. The method according to claim 10 wherein said first ceramic material comprises substantially the same ceramic composition as said second ceramic material.

12. The method according to claim 10 wherein the pore-forming additive comprises particles of polymethyl methacrylate.

13. The method according to claim 12 wherein the particle size of said particles of polymethyl methacrylate is from about 10 microns to about 100 microns in average diameter.

14. The method according to claim 12 wherein the particle size of said particles of polymethyl methacrylate is from about 20 microns to about 30 microns in average diameter.

15. The method according to claim 12 wherein the weight percent of said particles of polymethyl methacrylate is from about 10 weight percent to about 90 weight percent of the total weight of said second ceramic material.

16. The method according to claim 10 wherein said sintering is carried out at a temperature from about 1320 °C to about 1420 °C.

17. A method for forming a highly porous open cell foam structure comprising:

preparing a metallic open cell foam structure wherein said structure comprises a three dimensional array of interconnected micro-rods forming the edges of the open cells of said open cell structure;

oxidizing the surface of said micro-rods to form a porous surface microstructure on the outer layer of said micro-rods, and

reducing said porous surface microstructure with hydrogen to form a highly porous metallic open cell foam structure.

18. The method according to claim 17 wherein said highly porous metallic open cell foam structure comprises copper.

19. The method according to claim 17 wherein said oxidizing occurs in air at a temperature from about 300 °C to about 800 °C.

20. The method according to claim 17 wherein said reducing occurs in air at a temperature from about 400 °C to about 600 °C.

21. A method for catalyzing chemical reactions comprising:

catalyzing a chemical reaction with a highly porous open cell foam structure;

wherein said highly porous open cell foam structure has a three dimensional array of interconnected micro-rods forming the edges of the open cells of said open cell structure, said micro-rods having an inner core integrally bonded to a porous outer layer, said inner core comprising a first material and said porous outer layer comprising a second material and wherein said second material has a substantially higher porosity than said first material.

22. The method according to claim 21 wherein said highly porous open cell foam structure comprises copper.

23. The method according to claim 21 wherein said highly porous open cell foam structure comprises porcelain.

24. The method according to claim 21 wherein said catalyzing comprises catalyzing the conversion of CO to CO₂.

25. The method according to claim 21 wherein said catalyzing comprises oxidizing hydrogen to form water.

26. A catalyst system comprising:

a catalyst support;

a carrier layer on said catalyst support;

and

a catalyst coated on said support layer;

wherein said catalyst support comprises an open cell foam structure having a three dimensional array of interconnected micro-rods forming the edges of the open cells of said open cell structure, said micro-rods having an inner core integrally bonded to a porous outer layer, said inner core comprising a first material and said porous outer layer comprising a second material, wherein said second material has a substantially higher porosity than said first material.

27. The catalyst system of claim 26 wherein said micro-rods comprise nickel.

28. The catalyst system of claim 26 wherein said micro-rods comprise chromium.

29. The catalyst system of claim 26 wherein said carrier layer comprises γ -aluminum oxide.

30. The catalyst system of claim 26 wherein said catalyst comprises platinum.

31. The catalyst system of claim 26 wherein said catalyst comprises rhodium.

32. A highly porous open cell foam structure comprising:

an open cell foam structure having a three dimensional array of interconnected micro-rods forming

the edges of the open cells of said open cell structure, said micro-rods having an inner core integrally bonded to a porous outer layer, said inner core comprising a first material and said porous outer layer comprising a second material wherein said first material comprises substantially the same ceramic or metallic composition as said second material, wherein said first material has a porosity from about 0.5% to about 10% and said second material has a porosity from about 20 to about 80%, wherein said micro-rod has a thickness from about 0.1 mm to about 3.0 mm and wherein said inner core has a thickness from about 60% to about 80% of the total micro-rod thickness and said porous outer layer has a thickness from about 40% to about 20% of the total micro-rod thickness.

33. The highly porous open cell foam structure of claim 32 wherein said micro-rods comprise copper.

34. The highly porous open cell foam structure of claim 32 wherein said micro-rods comprise porcelain.

35. The highly porous open cell foam structure of claim 32 wherein said micro-rods comprise nickel.

36. The highly porous open cell foam structure of claim 32 wherein said micro-rods comprise chromium.

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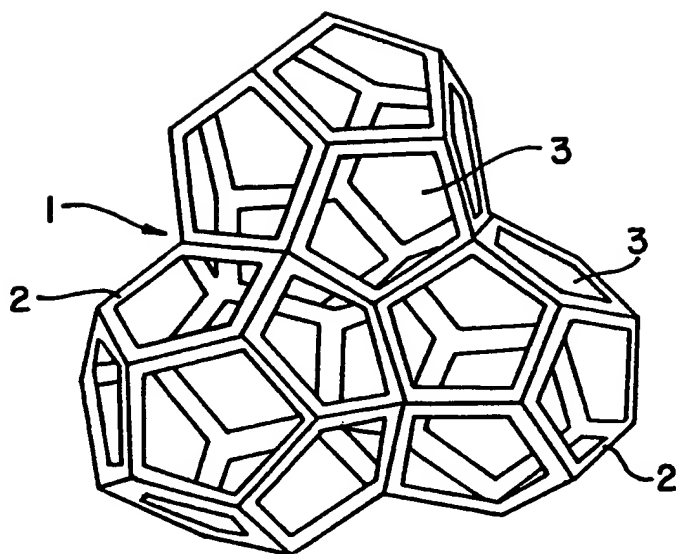


FIG. 1

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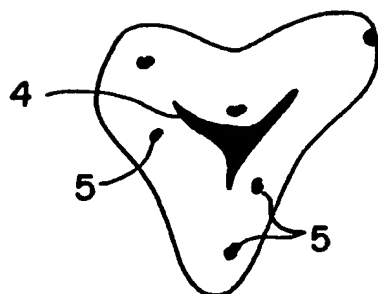


FIG. 2(a)

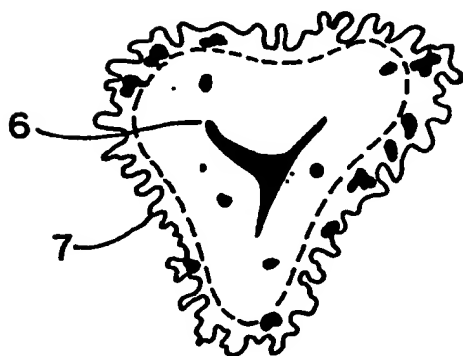


FIG. 2(b)

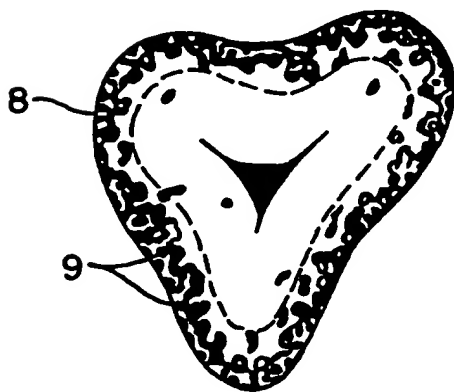


FIG. 2(c)

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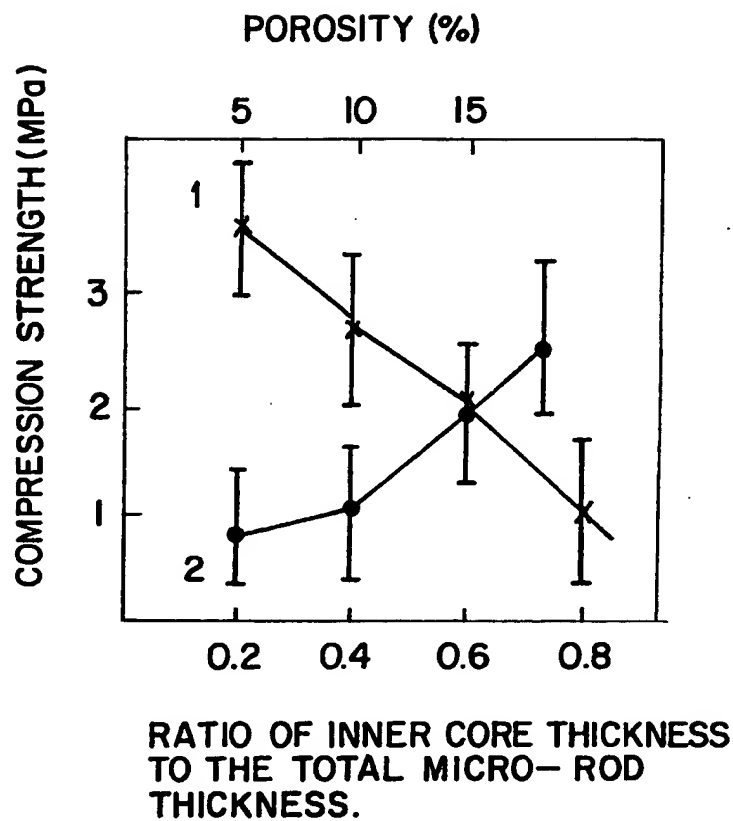


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/10308

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : 502/244, 245,259, 261, 439, 527; 423/247; 419/2,36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/244, 245,259, 261, 439, 527; 423/247; 419/2,36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A 4,569,821 (Duperray et al.) 11 February 1986, (Note claims 1-20)	1-20,26-36
Y	US,A 3,895,917 (Ravault) 22 July 1975 (Note columns 1-4)	1-36
Y	US,A 3,408,180 (Winkler) 29 October 1968 (Note complete patent)	1-20,26-36
A	US,A 3,946,039 (Walz) 23 March 1976 (Note column 1)	1-16,26-36
Y	US,A 4,465,789 (Lindsley) 14 August 1984 (Note Example 2)	1-23,24-36
A	US,A 4,495,308 (Gibson) 22 January 1985	1-36



Further documents are listed in the continuation of Box C.



See patent family annex.

Special categories of cited documents:		T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A	document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E	earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O	document referring to an oral disclosure, use, exhibition or other means		
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

02 FEBRUARY 1994

Date of mailing of the international search report

21 MAR 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10308

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A 3,565,830 (Keith et al), 23 February 1971	1-36

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10308

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (5):

B01J 21/12, 21/04, 23/26, 23/40, 23/72, 23/89, 35/10; C01B 31/18; B22F1/00